

Drop-photochemical deposition of aluminum oxide thin films from aqueous solutions

Shunta Sato and Masaya Ichimura

Department of Engineering Physics, Electronics and Mechanics, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan

e-mail : ichimura.masaya@nitech.ac.jp

Abstract

Aluminum oxide thin films were deposited onto fluorine-doped tin oxide-coated glass by drop photochemical deposition for the first time. The deposition solution was deionized water containing aluminum sulfate and sodium thiosulfate. Small amount of the solution was dropped on the substrate and irradiated with UV light. The solution was replaced with new one after 5 min irradiation, and the process was repeated 10 times. A film was not deposited without thiosulfate ions in the solution. The deposited films were transparent, and their band gap was larger than 4 eV. The O/Al composition ratio was about 1.2, smaller than the stoichiometric ratio 1.5.

Keywords

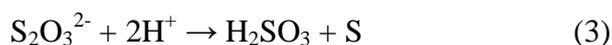
aluminum oxide, thin film, photochemical deposition

1. Introduction

Aluminum oxide (Al_2O_3) films attracted great interest due to their excellent physical and chemical properties, such as large band gap (8.7 eV), high dielectric constant (~ 9), and high chemical and thermal stability [1-3]. Nonstoichiometric AlO_x films also have those merits and were employed for protective or passivation coatings in variety of devices, including microelectronics, solar cells, and display devices [4, 5]. So far, to prepare aluminum oxide thin films, various methods were used such as atomic layer deposition [2], chemical vapor deposition [6], pulsed laser deposition [7], plasma enhanced chemical vapor deposition

[8], solvothermal deposition [9], DC reactive magnetron sputtering [10], as well as sol-gel deposition [11]. Recently, AlO_x thin films were also deposited by electrochemical deposition (ECD) using aqueous solutions containing aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) [12]. In ECD of AlO_x , it was reported that sodium thiosulfate is necessary to deposit films. A metal sulfide is usually deposited by ECD from an aqueous solution containing metal ions and thiosulfate ions. However, aluminum sulfide is not stable in water and easily oxidized. Thus AlO_x was deposited rather than AlS_x by ECD.

In the present study, AlO_x thin films are deposited by the photochemical deposition (PCD) technique using the same solutions as for ECD, for the first time, to the best of our knowledge. In PCD, a compound is synthesized by the photochemical reactions in the deposition solution and deposited on the substrate [13, 14]. The advantages of PCD are its simplicity, low cost, good controllability, and capability of large area deposition. The deposition is a chemical process in an aqueous solution, and thus there should be no damage on the sample surface. Moreover, while ECD can be applied only for a conductive substrate, an insulating substrate can also be used in PCD. So far, PCD was successfully applied for sulfide deposition. For example, ZnS is formed by the following photochemical reactions in an aqueous solution.



Many metal sulfides can be formed by similar reactions. If we apply this technique for aluminum, one can expect that AlO_x will be obtained rather than AlS_x , as in the case of ECD, because AlS_x will be readily oxidized in water.

In the original PCD, the substrate was immersed in the stirred solution and irradiated with UV light as shown in Fig. 1. Thus a significant part of synthesized compound molecules will drift away and not adhere to the substrate. Moreover, if the reactions are vigorous, the solution becomes hazy and a part of the light does not reach the substrate. To avoid those difficulties, we adopted the drop-PCD technique [15]. Figure 2 shows schematic of the drop PCD apparatus. In drop-PCD, a small amount of the solution was dropped on the substrate and photo-irradiated. When the solution becomes hazy, it is removed and replaced with fresh one. This technique was successfully applied for SnO_2 deposition, and it was reported that the film adhesion was much improved compared with ordinary PCD [15]. Details of the

deposition are given in the next section, and characterization results are given in the third section.

2. Experimental

AlO_x thin films were deposited onto fluorine-doped tin-oxide-coated glass (FTO-glass) substrates from an aqueous solution. The solutions contained 5 mM aluminum sulfate $\text{Al}_2(\text{SO}_4)_3$ and 0-100 mM sodium thiosulfate $\text{Na}_2\text{S}_2\text{O}_3$ with unadjusted pH (~4.2). To prepare the deposition solution, the solution of aluminum sulfate was prepared firstly. The aluminum sulfate was added to a hot water (80°C) with a stirring. After the solution became clear, the solution was cooled down to room temperature. Then the sodium thiosulfate was added to it. In drop-PCD shown in Fig. 2, the films were deposited by dropping a small amount of the solution (about 0.25 mL over an area of $18 \times 18 \text{ mm}^2$) onto the substrate, which was irradiated with the UV light of an ultrahigh-pressure mercury arc lamp. The total irradiation power was about 500 mW/cm^2 . The irradiation time was 5 min, and then the substrate was cleaned by deionized water and dried. The thin films were fabricated by repeating the process 10 times. For comparison, ordinary PCD, shown in Fig. 1, was also performed using the same solution. The substrate was immersed in the solution at a depth of 2-3 mm from the solution surface, and irradiated with the light of an ultrahigh-pressure mercury arc lamp. The irradiation power was 870 mW/cm^2 , and the deposition period is 1 h. Annealing was performed at 200 °C in N_2 ambient for 60 min.

The compositional analysis of the deposited films was carried out using the model JEOL JAMP 9500F Auger microprobe at probe current 2×10^{-8} A and voltage 10 kV. An argon-ion etching with acceleration current 20 mA and voltage 3 kV was employed to sputter the film surface. Scanning electron microscope (SEM) images with the magnification of 5000 were also taken using JAMP 9500F. The optical transmittance measurement was performed using the JASCO U-570 UV/VIS/NIR spectrometer with the FTO substrate as the reference. Raman spectra excited by a 633 nm red laser were collected using Raman spectrophotometer NRS-3300 (JASCO). The chemical states of elements in the sample were analyzed by X-ray photoelectron spectroscopy (XPS) using PHI5000 VersaProbe with the standard C 1s peak at 285.0 eV as a reference for correcting the shifts. The argon-ion etching was employed to sputter the film surface. The film thickness was measured by an Accretech Surfcom-1400D profile meter.

3. Results and discussion

Figure 3 shows the dependence of the film thickness on the $\text{Na}_2\text{S}_2\text{O}_3$ concentration for drop-PCD (squares). Since the film was not deposited without $\text{Na}_2\text{S}_2\text{O}_3$, thiosulfate ions are necessary to deposit a film as in the case of ECD [12]. Thus, the reactions of AlO_x -PCD will be as follows. Thiosulfate ions act as a reducing agent by reaction (1), and also act as a sulfur source according to reactions (2) and (3). Then, AlS_x is formed firstly by the reaction similar to reaction (4) and then oxidized in water to form AlO_x . However, it is possible to consider another reaction: AlO_x can be directly formed with e^- released from thiosulfate ions and oxygen dissolved in the solution.



In order to clarify which mechanism is dominant, we attempted to deposit AlO_x by using 20 mM sodium sulfite Na_2SO_3 instead of sodium thiosulfate $\text{Na}_2\text{S}_2\text{O}_3$. Sulfite ions act as a reducing agent like thiosulfate ions under UV irradiation, without releasing sulfur [16], but no film was deposited with sodium sulfite. Therefore, sulfur would be necessary to deposit AlO_x thin films by PCD. This indicates that the sulfide would be first formed and then converted to the oxide in the PCD process of AlO_x . According to Fig. 3, the thickness is largest when the $\text{Na}_2\text{S}_2\text{O}_3$ concentration is 20 mM. Thickness decrease at higher concentration is attributed to the solution becoming hazy as a consequence of the vigorous reaction.

The ordinary PCD method was also carried out for comparison, and the obtained film thicknesses were also plotted in Fig. 3 (circles). The maximum film thickness was 0.02 μm , i.e., about five times smaller than for drop-PCD, in spite of the higher irradiation power. This shows that adhesion of the reaction products to the substrate was much improved in drop-PCD compared with ordinary PCD.

In the following, characterization results are shown for the films deposited by drop-PCD with 50 mM $\text{Na}_2\text{S}_2\text{O}_3$. Figure 4 shows Auger electron spectroscopy (AES) spectra before and after the annealing at 200°C. The AES spectra show high Al and O signals with a small S signal. The elemental composition was estimated using the standard relative sensitivities of elements [17]. The obtained O/Al ratios for both the films are about 1.2. This means that the deposited films were not Al_2O_3 but AlO_x , with x less than the stoichiometric ratio 1.5. A weak sulfur signal was also observed; but its intensity was non-uniform within a sample, and variation among the samples was also significant. Generally, the obtained S/Al ratios are in the range of 0 - 0.04 for the as-deposited film and tend to become smaller after the annealing. We found no significant difference in composition between the samples deposited with different $\text{Na}_2\text{S}_2\text{O}_3$ concentrations.

The SEM image of the surface of the as-deposited film is shown in Fig. 5. The film is continuous with some particles on its surface. In the Raman measurement, only the peaks due to elemental sulfur were observed, and their intensities were rather non-uniform within a sample surface. The absence of Al-O signals would be due to their low scattering efficiency. On the other hand, elemental sulfur absorbs visible light and has a high Raman scattering efficiency for the red light (633 nm). After the annealing, the Raman peaks due to elemental sulfur tend to be reduced.

The optical transmittance spectra of the deposited films are shown in Fig. 6. In the visible region, the transmittance is about 80 % for both the as-deposited and annealed films. The transmittance of the as-deposited films is about 60-70 %, smaller than that of the annealed film, in the UV range. The film thicknesses of both samples were almost the same. It seems that the optical transmittance of the as-deposited film is affected by absorption due to elemental sulfur and scattering due to surface roughness (particles). There is no absorption edge in the figure, and thus the band gap of the deposited films is larger than 4 eV. We were not able to measure the optical transmittance at shorter wavelength because the FTO substrate is opaque. Therefore, the band gap of the deposited films was not evaluated. The absorption edge was absent in the spectra for the samples deposited under the other conditions.

The XPS spectra of the Al 2p peak and S 2p peak for the as-deposited film are shown in the Figs.7 (a) and (b), respectively. The broad and asymmetric peaks will be due to overlap of the various peaks and are here fitted with two or three Gaussian curves. For the Al 2p peak, the lower binding energy peak located at 74.8 eV is attributed to Al_xO_y , while the higher peak at 75.5 eV is attributed to Al^{3+} ion in Al_2O_3 [18]. For the S 2p peak, the lowest binding energy peak located at 168.3 eV is attributed to SO_3 peak. The other peaks at 169.3 eV and 170.5 eV are attributed to SO_4 (S 2p_{3/2}) and SO_4 (S 2p_{1/2}), respectively. Although the elemental sulfur peaks were observed in the Raman measurement, there are no peaks attributed to elemental sulfur in the XPS spectra; this is attributed to the high Raman efficiency of elemental sulfur, whilst sulfate or sulfite cannot show this effect. Thus, the amount of elemental sulfur is in fact relatively small, and the sulfur in the films is mainly attributed to a residue of the deposition solution since the solution contains $\text{Al}_2(\text{SO}_4)_3$ and $\text{Na}_2\text{S}_2\text{O}_3$.

Since the O/Al ratio is smaller than 1.5, the films will contain oxygen-deficiency defects, which could act as a donor. For a future study, the deposited films will be annealed in various ambient (oxidizing or reducing) at higher temperatures, and their electrical properties will be characterized.

4. Conclusion

AlO_x thin films have been deposited onto FTO glass from a solution containing aluminum sulfate and sodium thiosulfate by drop-PCD. Thiosulfate ions are necessary to deposit the films. According to the AES measurement, O/Al ratio is smaller than the stoichiometric composition ratio of 1.5. The film transparency in the visible range becomes better after annealing, and the band gap is larger than 4 eV.

References

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Figure Captions

Fig.1. Schematic of the photochemical deposition.

Fig.2. Schematic of the drop photochemical deposition.

Fig.3. Dependence of the deposited film thickness on $\text{Na}_2\text{S}_2\text{O}_3$ concentration. Squares: drop-PCD (Fig. 2), circles: ordinary PCD (Fig. 1).

Fig.4. AES spectra for the as-deposited and annealed films.

Fig.5. SEM images for the as-deposited film.

Fig.6. Optical transmittance measurements for the as-deposited and annealed films.

Fig.7. XPS peaks of (a) Al 2p and (b) S 2p for the as-deposited film with the fitted Gaussian curves.

Figure 1:

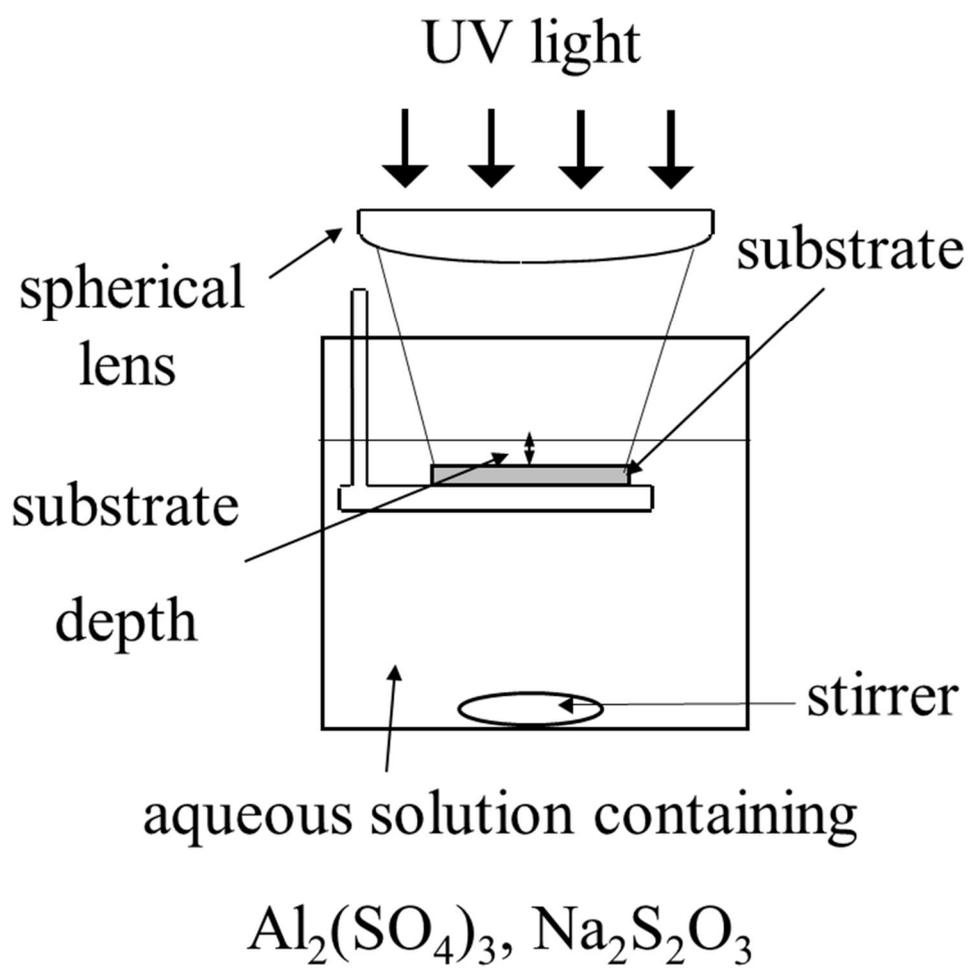


Figure 2:

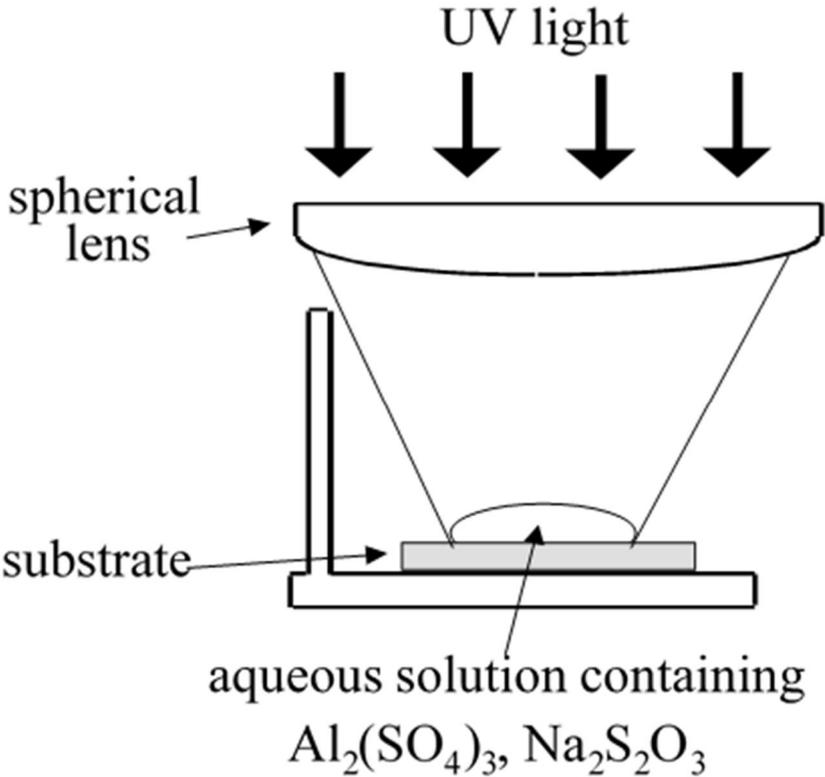


Figure 3:

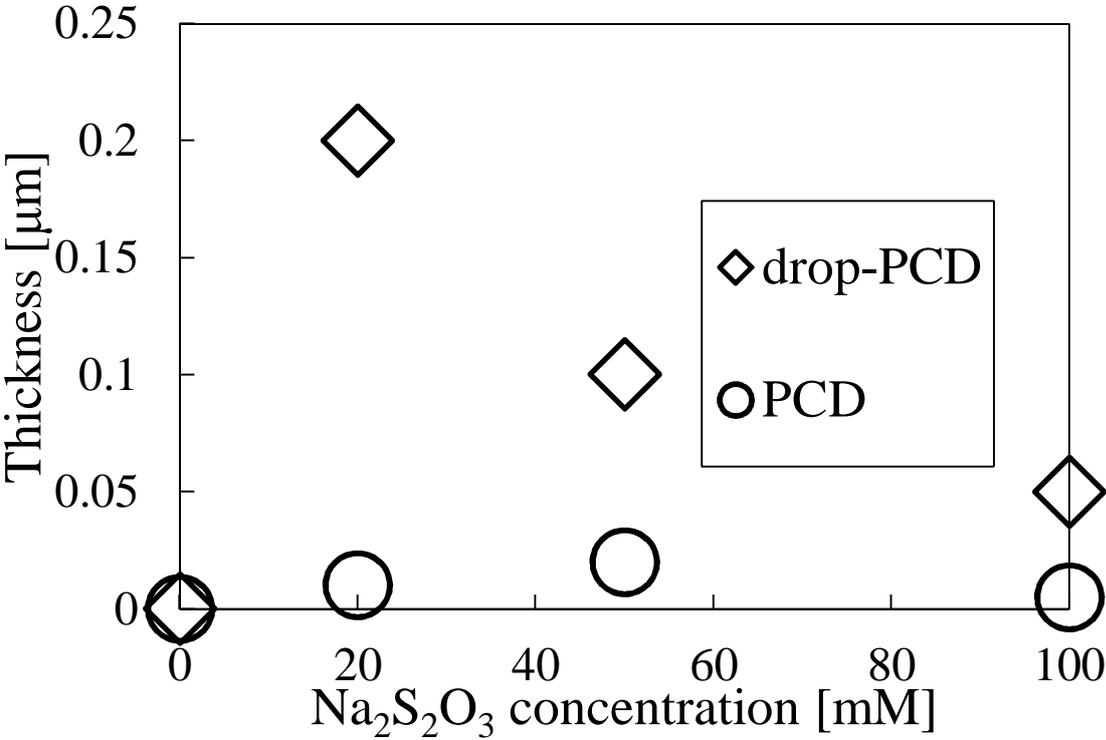


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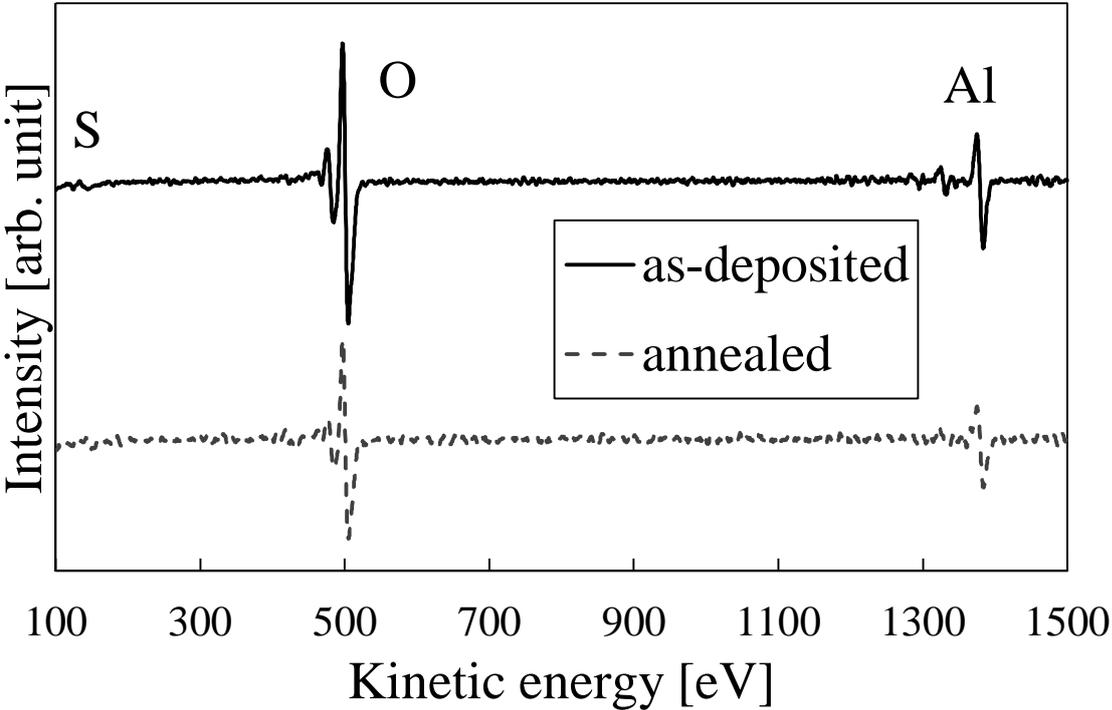


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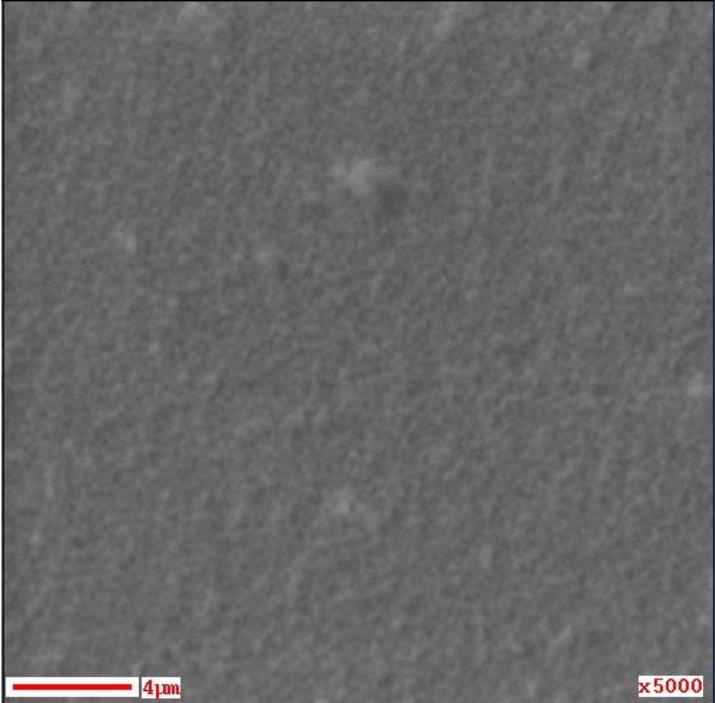


Figure 6:

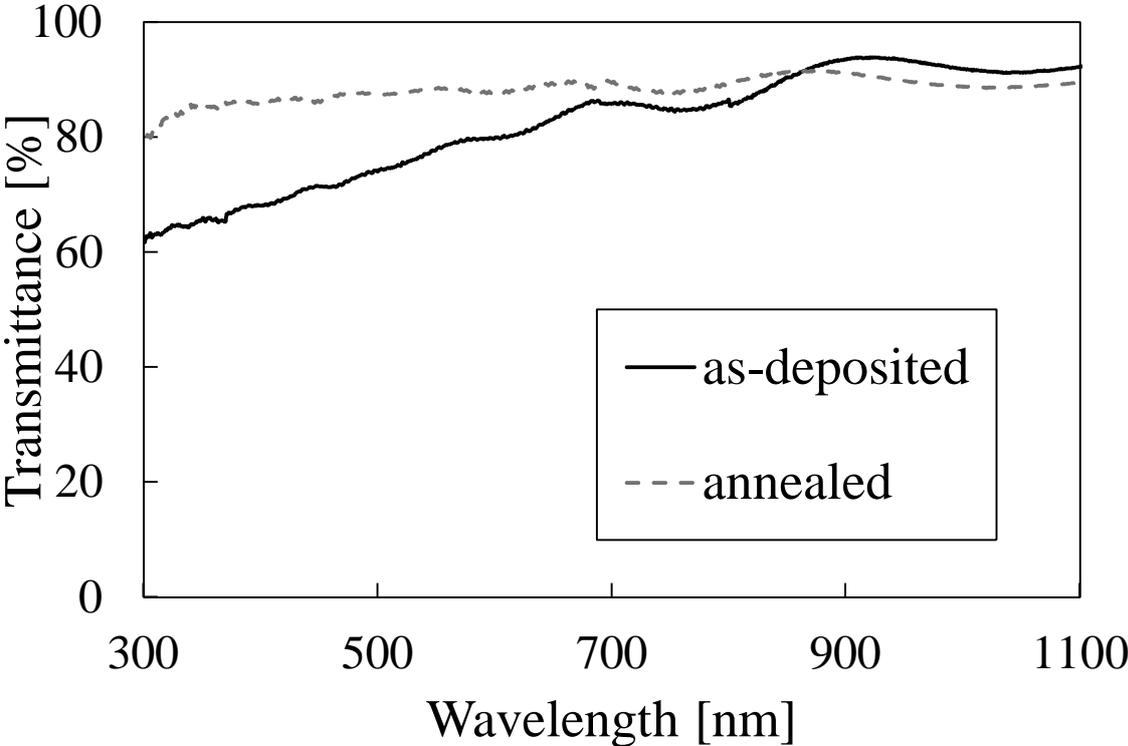
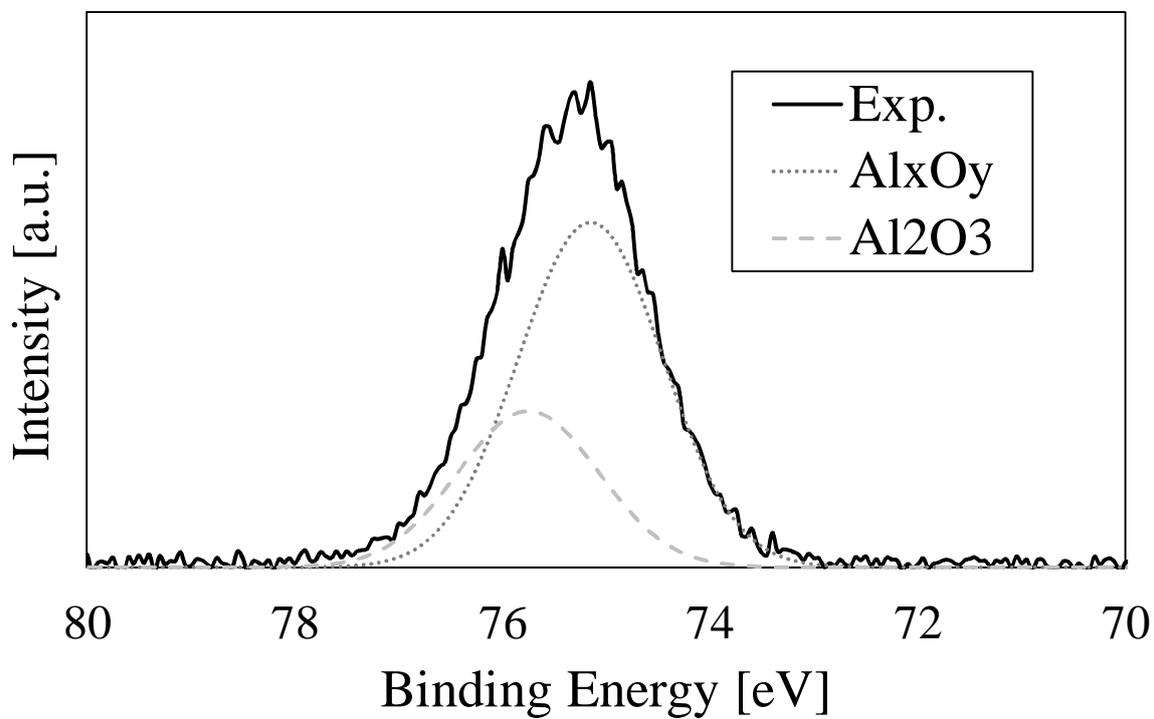
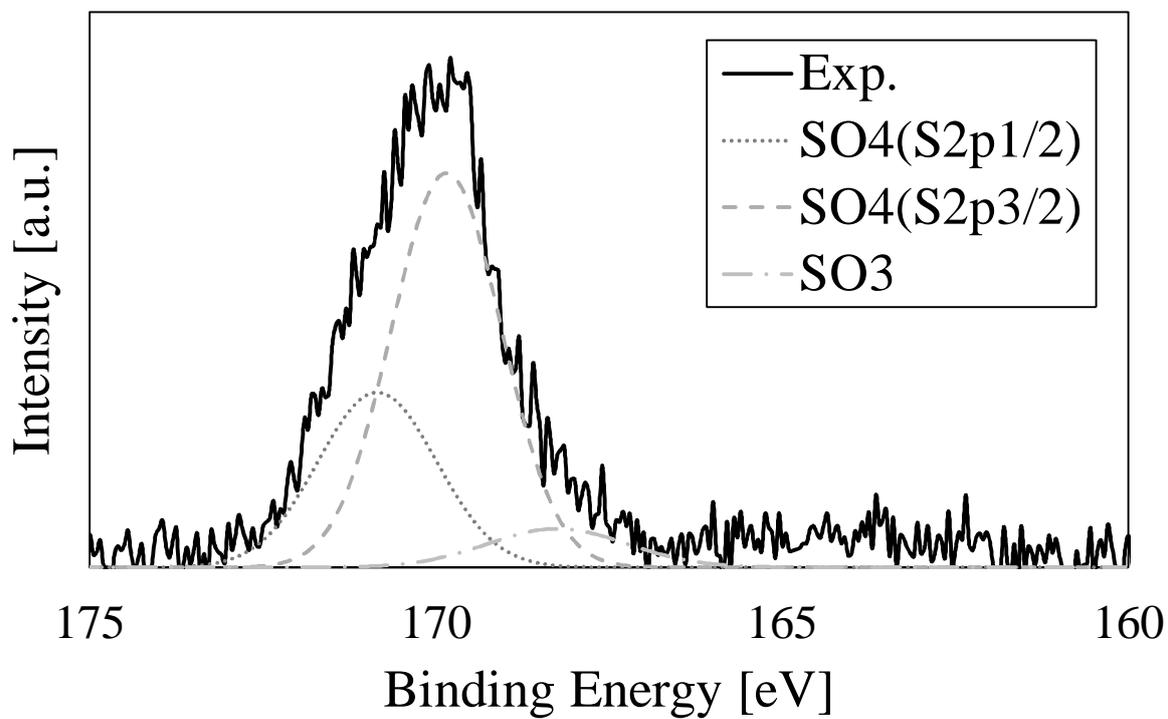


Figure. 7:



(a)



(b)